III.A.10 SOFC Compressive Seal Development at PNNL

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Objectives

- Develop inexpensive seals for solid oxide fuel cell (SOFC) stacks that offer low leak rates and excellent reliability during long-term operation and thermal cycling.
- Improve understanding of degradation mechanisms affecting seal performance, including intrinsic materials degradation in the SOFC environment and interactions with other SOFC components.

Approach

- Perform preliminary evaluation of seal concepts.
- Prepare and test seal materials and designs under SOFC-relevant conditions (atmosphere and temperature).
- Evaluate tested seal components to improve understanding of degradation processes during seal operation.

Accomplishments

- Developed inexpensive "hybrid" compressive seal based on mica paper with glass-ceramic interlayers.
- Demonstrated low leak rate and stability of hybrid seals during long-term testing with extensive thermal cycling.

Future Directions

- Complete investigation of long-term seal performance/reliability.
- Evaluate and optimize mica/glass "composite" version of hybrid seal.
- Study degradation and reactions at mica/interconnect interfaces during aging in SOFC environments.

Introduction

Planar SOFC stacks require adequate seals between the interconnect and cells in order to prevent mixing of the oxidant and fuel gases and to prevent leaking of gases from the stack. In addition, these seals must also allow the stack to be thermally cycled repeatedly (between ambient conditions and the operating temperature). Several different approaches to sealing SOFC stacks are available, including rigid, bonded seals (e.g., glass-ceramics); compliant seals (e.g., viscous glass); and compressive seals (e.g., mica-based composites). Rigid seals typically soften and flow slightly during stack fabrication (at a temperature above the operating temperature) but then become rigid (to avoid excessive flow or creep) when cooled to the operating temperature. The thermal expansion of rigid seals must be closely matched to the other stack components in order to avoid damaging the stack during thermal cycling. Compliant seals attempt to simultaneously perform the sealing function and prevent thermal stress generation between adjacent components. Compressive seals typically utilize materials such as sheet-structure silicates that do not bond adjacent SOFC components; instead, the sealing material acts as a gasket, and gas-tightness is achieved by applying a compressive force to the stack. Both compliant and compressive seals potentially improve the ability of the stack to tolerate thermal expansion mismatch between the various stack components.

Previous Core Technology Program seal development work at Pacific Northwest National Laboratory (PNNL) has focused on a novel "hybrid" mica-based compressive seal concept. Initial development efforts focused on hybrid seals based on naturally cleaved Muscovite mica sheets, which offered leak rates several orders of magnitude lower than those measured with "plain" mica compressive seals. The seals, however, did not exhibit the desired thermal cycle stability as the leak rates tended to increase with increasing thermal cycles. Microstructural characterization of cycled seals revealed undesirable degradation of the Muscovite mica due to coefficient of thermal expansion (CTE) mismatch with the mating materials. Improvements in thermal cycle stability have been obtained with seals based on Phlogopite mica paper, which has a higher "x-y" CTE (~11 ppm/°C) than Muscovite mica (~7 ppm/°C). Recent seal work has focused on optimizing Phlogopite paper-based hybrid seals to maintain low leak rates during thermal cycling under reduced applied compressive loads (6 to 100 psi).

Approach

Candidate seals were evaluated by studying seal quality (i.e., leak rate or open circuit voltage) as a function of temperature, gas pressure and composition, and applied compressive load. For leak rate measurements, the seal assemblies were placed between an Inconel600 pipe and an alumina substrate. A compressive load was applied throughout the tests, including the heating and cooling cycles. The leak rates were determined with high-purity helium, maintaining a 2 psi differential. Thermal cycling was conducted between 100°C and 800°C, with 2-hour dwells at 800°C. Open circuit voltage (OCV) tests were also conducted using electroded dense 8YSZ electrolyte pressed between an Inconel cap and an alumina base support; in these tests, the mica seals were located between the 8YSZ and the Inconel fixture. Stability and resistance to chemical interaction with other SOFC components were evaluated through thermogravimetric analysis, x-ray diffraction, electron microscopy, and optical microscopy.

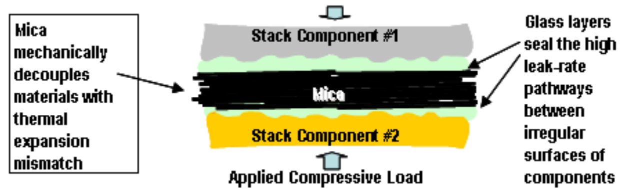

Figure 1. Schematic Illustration of Hybrid Mica Seal; Mica paper is in center of seal with glass layers on each side to fill mica/stack component interfaces

Results

The glass-mica paper hybrid seals consist of commercially available Phlogopite mica paper sandwiched between thin layers of a proprietary SOFC glass-ceramic seal material covered under United States Patents 6,430,966 and 6,532,769. The seals were fabricated by inserting the mica paper between polymer tapes (prepared by conventional tape casting techniques) which contained the glass-ceramic powder. Sealing was accomplished by placing the tri-layer tape/mica/tape structure between the stack components to be sealed. The configuration was subsequently heat-treated (typically to 830ºC) to soften the glass sufficiently to cause bonding to the component surfaces. Final seal thickness was typically ~100-200 µm (Figure 1).

Performance

Results for thermal cyclic leak rate tests on a 2"x 2" hybrid seal (1 layer of mica paper sandwiched between glass-ceramic surface layers) are shown in Figure 2. When compressed at ~25 psi or more, the seals exhibited extremely low leak rates and excellent stability during repeated thermal cycling. It is important to emphasize that, in these tests, the materials adjacent to the seal had a significant CTE mismatch (Inconel600, with a CTE of ~16-17 ppm/K, vs. alumina, with a CTE of ~8-9 ppm/K). As a point of comparison, similar tests using a glass-ceramic seal alone between these materials resulted in seal failure after a single thermal cycle.

Results for OCV testing of a 2"x 2" seal compressed at 100 psi are shown in Figure 3. The OCV measurements were conducted using dilute moist hydrogen "fuel" vs. air, for which the

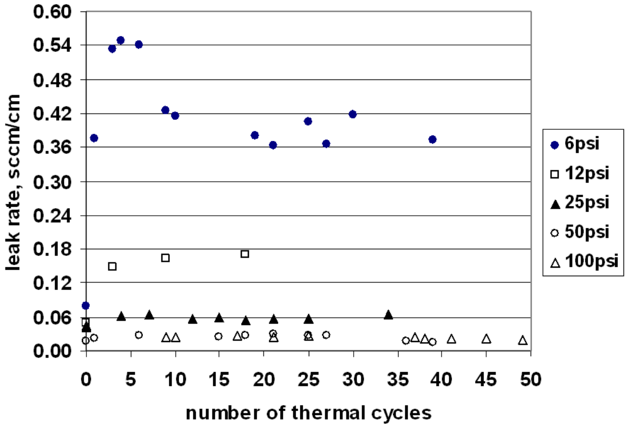

Figure 2. Leak Rates at 800ºC of a 2" x 2" Hybrid Phlogopite Mica Seal Pressed under Various Compressive Loads

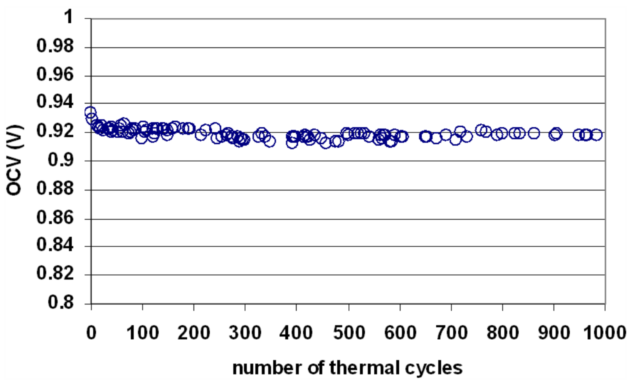

Figure 3. OCV Results for Thermal Cycle Tests on 2" x 2" 8YSZ Plate with Hybrid Phlogopite Mica Seal Compressed at 100 psi

calculated Nernst voltage at 800ºC is 0.932-0.934 V. Over 1000 thermal cycles (heated from 100ºC to 800ºC in 30 minutes), the OCV decreased by less than 2%.

It should be noted that the leak rates shown in Figure 2 were measured at 2 psid; reduction of the pressure drop across the seal results in a linear decrease in leak rate. A typical example is shown in Figure 4 for a 2"x 2" hybrid Phlogopite mica pressed at 12.5 psi; the data in Figure 4 were taken after 19 thermal cycles. For pressure drops of 0.1-0.2 psid, the seal leak rate was ~0.02 sccm/cm.

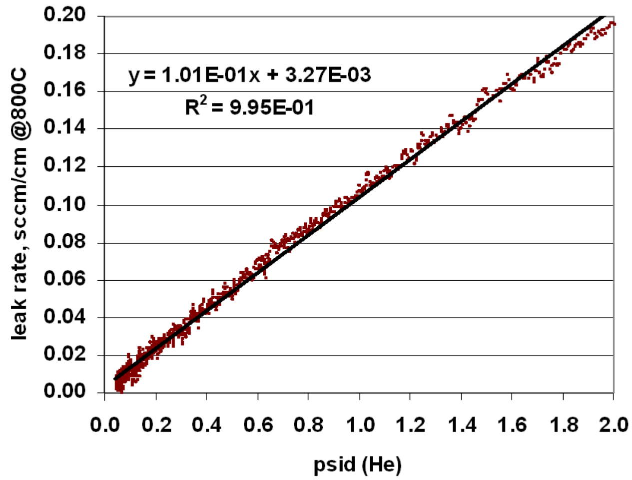

Figure 4. Effect of Differential Pressure on the Leak Rate of a 2" x 2" Hybrid Phlogopite Mica Seal Pressed at 12.5 psi; Measurement was taken after 19 thermal cycles

Conclusions

Inexpensive, easy-to-fabricate "hybrid" mica paper/glass compressive seals were found to offer stable, low leak rates under relatively low applied compressive stress during isothermal and thermal cyclic exposure conditions.

FY 2004 Publications

1. Y-S Chou, J. W. Stevenson, "Novel infiltrated Phlogopite mica compressive seals for solid oxide fuel cells," *Journal of Power Sources* (in press) (2004).

2. Y-S Chou, J. W. Stevenson, "Long-term thermal cycling of Phlogopite mica based compressive seal for solid oxide fuel cells," in Developments in Fuel Cells and Lithium Ion Batteries, *Ceramic Transactions* vol. 161 (2004), edited by Arumugan and Manthiram (in press).

3. Y-S Chou, J. W. Stevenson, "Infiltrated Phlogopite micas with superior thermal cycle stability as compressive seals for solid oxide fuel cells," in Developments in Fuel Cells and Lithium Ion Batteries, *Ceramic Transactions* vol. 161 (2004), edited by Arumugan and Manthiram (in press).

FY 2004 Presentations

1. J. W. Stevenson, P. Singh, K. Meinhardt, L. Chick, C. Coyle, Y-S Chou, S. Weil, and G. Yang, "SOFC seals: technology challenges and status," 28th International Cocoa Beach Conference, Symposium II: International Symposium on Solid Oxide Fuel Cell Materials and Technology, Cocoa Beach, Florida, 2004.

2. Y-S Chou and J. W. Stevenson, "Long-term thermal cycling and open circuit voltage testing of Phlogopite mica-based compressive seals for solid oxide fuel cells," 106th Annual Meeting of the American Ceramic Society, Indianapolis, Indiana, April 18-22, 2004.

3. Y-S Chou and J. W. Stevenson, "Infiltrated Phlogopite micas with superior thermal cycle stability as the compressive seal for solid oxide fuel cells," 106th Annual Meeting of the American Ceramic Society, Indianapolis, Indiana, April 18-22, 2004.

4. Y-S Chou, J. W. Stevenson, and P. Singh, "Development of compressive seals for solid oxide fuel cells," SECA CTP Program Review, Boston, Massachusetts, May 11-13, 2004.